Sulphur Dioxide Abetment Using Synthesized South African Limestone/Siliceous Sorbents

D. O. Ogenga, K. L. Lee, M. Mbarawa

Abstract- **This study presents experimental findings on the preparation and characterization of locally available fly ash, CaO obtained from calcination of limestone in a laboratory kiln at a temperature of 900ºC and CaO/ siliceous sorbent prepared using an atmospheric hydration process. The sorbent was prepared under different hydration conditions: CaO/ fly ash weight ratio, hydration temperature (55 – 75ºC) and hydration period (4-10 hours). The sorbents were then tested in a fixed bed reactor for the removal of SO₂ at 87 ºC and relative humidity of 50 %. The chemical composition of both the fly ash and calcined limestone had relatively high Fe₂O₃ and oxides of other transitional elements which provided catalytic ability during the sorbent sorption process. All the three hydration variables had both individual and interactive effects on SO₂ sorption capacity. Generally the sorbents had higher SO₂ absorption capacity compared to calcined limestone or fly ash alone. The sorbents had mesoporous structure larger pore volume and BET specific surface area than both calcined limestone and fly ash, the starting materials. The X-ray diffraction (XRD) analysis showed the presence of complex compounds containing calcium silicate hydrate in the synthesized sorbents.**

Keywords— **fly ash; desulphurization; hydration variables; calcined limestone; sorbents.**

I. INTRODUCTION

The fact that coal will be an important source of energy, and in particular in electric power generation, for sometime in the near future cannot be an overstatement. With fluctuations in crude oil prices and stability of coal prices coupled with its abundance and availability in almost all parts of the world will certainly increase its (coal's) usage [1]. Although technologies such coal gasification, fluidized bed combustion, selective non catalytic reduction and others would sufficiently address the issue of environmental concern in coal utilization, their implementation by especially developing countries is obviously still a mirage. This means pulverized coal combustion (PCC) will for sometime widely be used. Use of PCC requires use of post combustion flue gas control technologies in order to reduce SO_2 from being released into the atmosphere. Consequently, emissions control measures of gas pollutants such as SO_2 is

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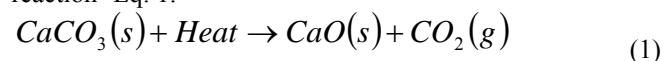
of utmost necessity. This means development of an efficient dry FGD technology using ash will be very beneficial to these nations.

Although dry flue gas desulfurization (FGD) technology has been argued to be more advantageous than the wet FGD processes in terms of capital cost and waste handling, the conversion of the sorbent is low. Increasing the utilization of lime in semi-dry /dry FGD systems is one of the current challenges researchers have to deal with [2, 3]. Fly ash, a pozzolanic material whose main components are usually SiO_2, Al_2O_3, and Fe_2O_3 [4], has shown good results when used to condition quicklime in a hydration process. The chemical composition of both the major and minor components in fly ash varies from one report to another depending on the parent coal composition [2, 5, 6, 7, 8]. This is also the same case with limestone from which quicklime when produced for hydration with fly ash during sorbent synthesis. Besides since fly ash contains both quartz and amorphous silica and the amorphous silica being more active than the crystalline quartz during pozzolanic reaction [9], the amount of the amorphous silica in the fly ash can thus have an effect on the resultant sorbent. It is therefore possible that South African calcined limestone/siliceous materials could have unique properties in the removal of SO_2 from flue gas. In this work, sorbents synthesized from calcined limestone conditioned with fly ash both of South African origin have been characterized and sulfated in order to investigate their influence in SO_2 absorption capacity.

II. MATERIALS AND METHODS

A. Materials and Methods

The starting materials for the preparation of sorbents were coal fly ash and limestone which obtained from different local power plants. These materials were physically characterized as shown in Table 1. The limestone was weighed, put in crucibles and then placed in the furnace where it was heated at 900 °C in the absence of air for 4 hours. The cooled sample was weighed in order to determine the weight loss due formation of vapour and CO_2. The average weight loss was found to be 41% of the original weight before heating. Limestone was calcined in a laboratory furnace in order to obtain CaO according to the reaction -Eq. 1.

$$CaCO_3(s) + Heat \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

Table 1: The physical analysis of Fly ash (FA) and Calcined limestone (CaO)

Component	Percentage composition	
	Calined limestone	Fly Ash
Surface area (m^2/g)	4.78	3.30
BJH Volume (cm^3/g)	0.013	0.009
Average pore width (nm)	8.85	7.65

B. Sorbent Preparation

For the preparation of sorbents, a determined quantities of calcium oxide and fly ash making a total weight of 15g were added into 100ml of de-ionized water at $45\,^oC$ and stirred at 150 rpm for 10minutes then, ash was added in different amounts at different treatments to result in various ratios being tested (ratio of CaO to fly ash) and 3g calcium sulphate are then added to the slurry simultaneously. While the amount of ash was varied for every run, the amount of CaO was kept constant. The slurry is subsequently heated to the predetermined slurrying temperature and time in thermostatic a water bath with a shaker at 120 rpm in order for the hydration process to take place. The slurry was then dried in a vacuum oven at 105 °C until completely dried. The resulting sorbent (dried cake) obtained was crushed into powder form, pelletized, sieved into particle size range of 250 – 300 μm and then sealed in a bottle before using it for characterization and sulfation tests.

C. Physical and chemical analysis

C.1 BET surface area

The samples were degassed at 105ºC for 10 h in a degas pot of an adsorption analyzer in order to remove moisture and other contaminants prior to BET surface area measurement. The samples were characterized using low temperature (77.35 K) nitrogen adsorption isotherms measured over a wide range of relative pressures from 10^{-6} to 1 atm. The nitrogen adsorption, which is physical in nature, was performed on a Micromeritics ASAP 2020 surface area and porosity analyzer. The pore volume distribution was determined from nitrogen adsorption isotherm by the Barrett – Joyner – Halenda (BJH) adsorption curve using inbuilt program in Micromeritics ASAP 2020.

C.2 XRD Analysis

The samples were prepared for XRD analysis using a back loading preparation method. They were analyzed with a PANalytical X'Pert's Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation in a diffraction angle (2θ) range of 5 ^{o}- 89 ^{o}. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program).

The desulphurization tests were carried out in a laboratory flue gas desulfurization rig at the conditions similar to those of bag filter conditions in dry and semi-dry FGD processes. The process was carried out under isothermal conditions, that is, at constant temperature. A repeat of batch tests at different constant temperatures thereby generating sets of sorbent utilization data was used to investigate the influence of temperature in the process.

III. RESULTS AND DISCUSSION

A. Chemical Analysis

Fly ash had the oxides of Na, K, Fe, Ti and Mn which can influence the reaction of the sorbent with SO_2: Oxides of Na and K would result in the formation of NaOH and KOH which reacts with SO_2 to form sulphite salts reducing SO_2 from the flue gas (see Eq. 2).

$$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l) \qquad (2)$$
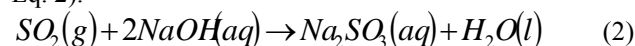
Existence of these oxides (Na and K) can however be disadvantageous as it will result in leachable wastes which will further cause environmental harm. The Oxides of Fe, Ti and Mn are expected to provide the catalytic ability to enhance the sulfation reaction between Ca in the sorbent and SO_2 [10]. For X-ray diffraction (XRD) analysis of the synthesized sorbent, the main phases were: $Ca-Al_2Si_4O_{12}.2H_2O$, SiO_2, $Ca(OH)_2$, $MgFeO_4$ and an amorphous phase (Fig. 1). The amorphous peak in the sorbent is suspected to be either unreacted silica or calcium silica hydrates which also exists in amorphous form [6]. The absence of strong peaks of SiO_2, alumina and CaO suggests that they reacted to form the calcium silicate hydrates and aluminate hydrates.

As widely reported in literature, these compounds are important in the formation of sorbents with increased specific surface area [3, 11]. In the presence of water during the hydration process the active silica and alumina in the siliceous materials reacts with hydrated lime to form complex compounds of calcium silicate / alluminate hydrate [3, 6, 12]. It is believed that these complex compounds are responsible for increased surface area of sorbents [11]. The high specific surface area is important for the accessibility of Ca^{2+} ions by SO_2 in the flue gas. Figure 2 shows the XRD patterns of fly ash in which the presence of peaks of $Al_6Si_2O_{13}$ and SiO_2 are observed. Fly ash consists of the amorphous silica hence the reason for the strong peaks of SiO_2 observed in the sample.

c- amorphous phase, b-$Ca(OH)_2$(portlandite), a- $Ca-Al_2Si_4O_{12}.2H_2O$, d-$MgFe_2O_4$, s - Silica (SiO_2),
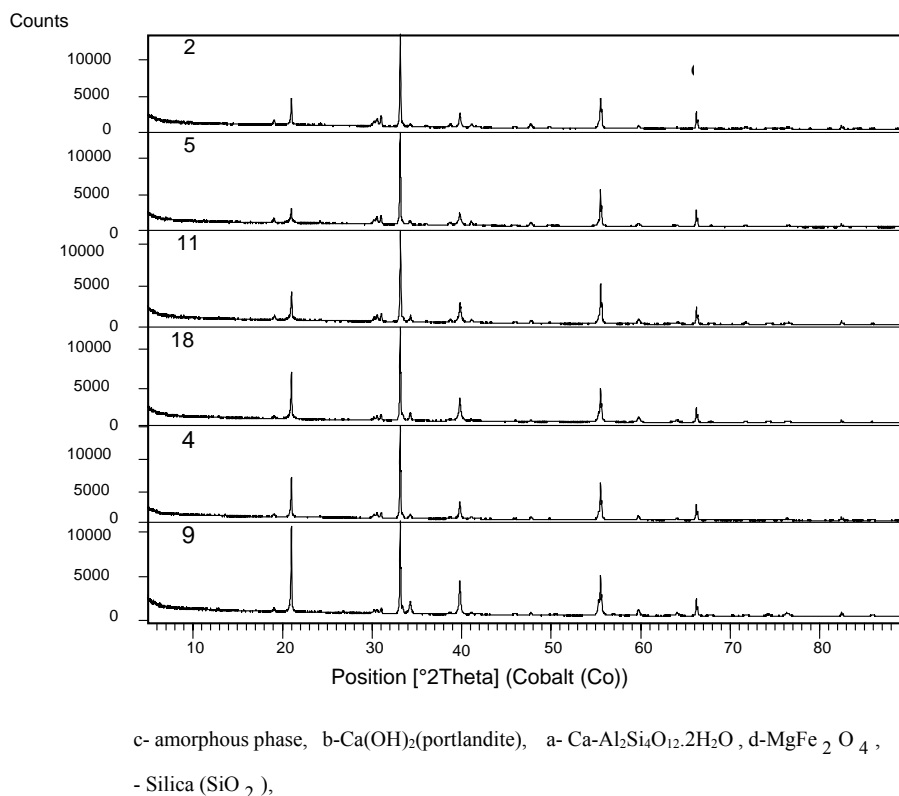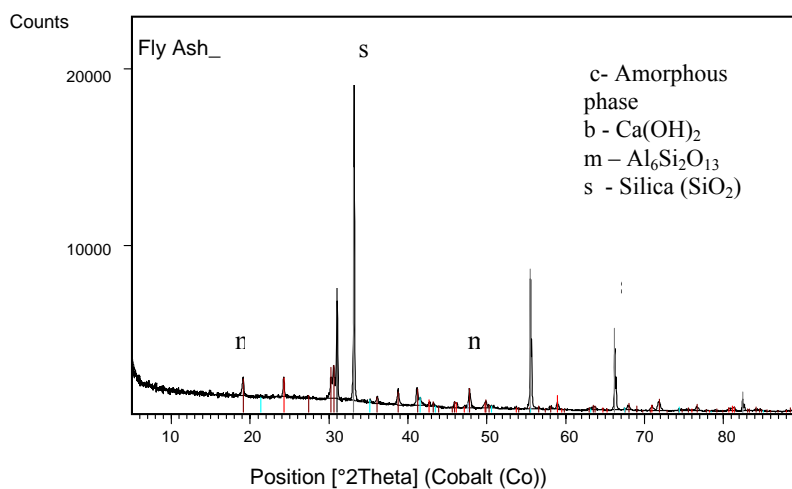
Figure 1: The XRD phases in (CaO) / Fly ash sorbent

Figure 2: The XRD phases in (CaO) / Fly ash sorbent

B. BET specific Surface area

The specific surface area of fly ash, calcined limestone and the synthesized sorbents are given in Table 2 with the general trend showing all the sorbents having higher surface area than the starting materials. The specific surface areas of the sampled synthesized sorbents ranged from 24.3 - 108.5 m^2/g. This indicates that the formation of calcium silicate hydrates and the presence of the amorphous Calcium silicate hydrates (CSH) could have been responsible for the increased surface area. The three hydration variables appeared to have both individual and interactive effects on the specific surface area of the sorbent. Of notable significance were hydration period and the amount of fly ash added. Increased hydration period and CaO /fly ash ratio resulted in higher specific surface area. It can be seen from the Table 3 that all the sorbents had mesopore type of pore structure with micropore structure not detectable. The mesopore is believed to responsible for the increased surface area. All the pore radii were within the range of 2 to 50 nm which as reported in literature has been found to be the effective zone for sulphation reaction of SO_2 and $Ca(OH)_2$/fly ash sorbents [11].

Table 2: BET specific surface area of the synthesized sorbents.

Sample	Hydration Temperature (K)	CaO/Fly ash Ratio	Hydration period (H)	Pore Radius (nm)	Specific surface area (m^2/g)
2	328	1.6	4	16.3	66.0
4	338	1.2	6	17.3	102.0
5	338	2.0	6	23.3	24.3
9	358	1.6	8	17.7	108.5
11	328	1.6	8	14.8	90.2
18	338	1.2	10	16.2	107.5

3.3 Sulfation

The sorbents were subjected to sulfation test at 87 ^{o}C, relative humidity of 50% and 2000 ppm SO_2 concentration. The activity results were monitored in the form of duration the sorbents take to maintain 100% removal of SO_2 per 0.1 g which was used for all the samples tested (Figure 3). Figure 3 shows the variation of the capacity of the calcined limestone /fly ash sorbents ability to maintain 100% SO_2 removal with the preparation (hydration) conditions. For the tested samples, the sorbent could afford up to 38 minutes of 100% removal. Although all the three hydration variables appeared to have individual influence on desulfurization activity, interactive effect was more significant. For instance at 65 ^{o}C, ratio of Calcined limestone to fly ash of 2.0 and 6 minutes hydration period, the time 100 % removal was 38 minutes which is the highest for the samples presented here.

IV. CONCLUSION

CaO/fly ash sorbents were prepared and characterized at different hydration periods and temperatures as well as weight ratios. Results showed that the specific surface area of CaO/ fly ash sorbents (24.3 - 108.5 m^2/g) was higher than that of the CaO (4.78 m^2/g) and fly ash (3.30 m^2/g) at all preparation conditions. The X-ray diffraction (XRD) analysis showed the presence of complex compound containing calcium silicate hydrate in the synthesized sorbents. This contributed to the high SO_2 removal. The sulfur dioxide removal was found to increase with an increase in the amount of fly ash with the ratio of 1:2 (CaO/ Fly ash) giving the highest value. It was also found that an increase in the hydration time as well as temperature resulted in an increase in desulfurization although the interactive effect of the three factors was more significant. Thus the use of these South African materials can substantially increase the specific surface area of South African limestones and the eventual calcium utilization in FGD applications.

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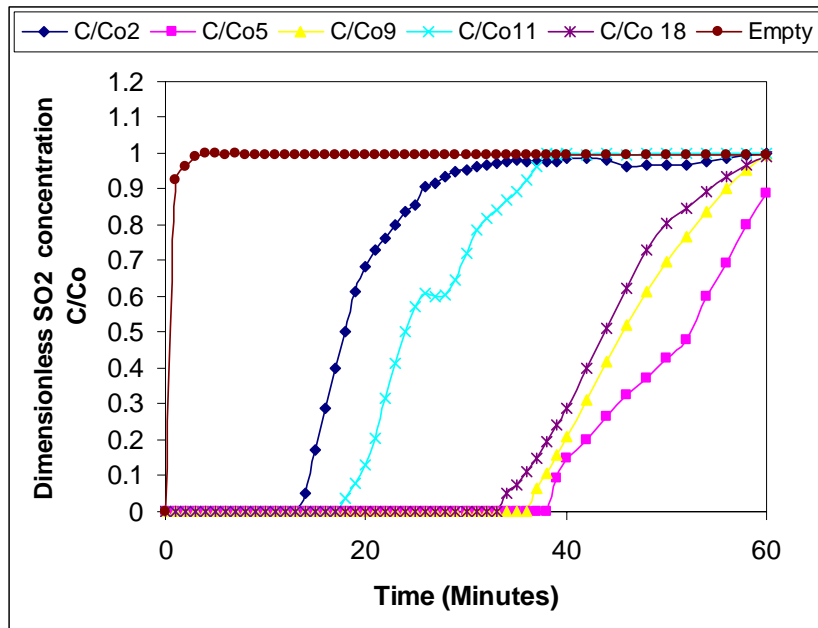
Figure 3: SO$_2$ Breakthrough curves for South African calcium/ siliceous sorbents furnace temperature 87 ^{o}C, relative humidity of 50% and SO$_2$ concentration 2000 ppm.